The insulator-metal transition in hydrogen

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In their pioneering work over 75 years ago, Wigner and Huntington (1) predicted that solid molecular hydrogen would dissociate and become an atomic metal when pressurized to 25 GPa (25 GPa = 0.25 megabar) at a temperature $T = 0$ K. Subsequently, one of the great challenges of condensed matter physics in the past and present century has been to achieve metallization of hydrogen. Theory and experiment have worked hand in hand. Hydrogen is conceptually the simplest of all atoms, with a single proton and electron, doubled in the molecule, yet it is extremely challenging to theorists. This is mainly because of the light mass, resulting in large zero-point motion (i.e., motion of the nuclei of a many-body solid at 0 K). To achieve the most accurate theoretical results, a full quantum mechanical analysis is required at all densities and conditions.

Following Wigner and Huntington (1), predictions of the metallization pressure (P) have ranged as high as 20 megabars and currently, are in the range of 4–6 megabars. This has been somewhat guided by experiment: the highest static pressures achieved with diamond anvil cells have been ~3.5 megabar, with hydrogen remaining an insulating molecular solid. Further predictions for metallic hydrogen are that it would be metastable (i.e., remain in the metallic state when pressure is released), may be a room temperature superconductor, and may even be a liquid at 0 K when compressed to the atomic metallic state. To test these predictions, a statically compressed sample at modest temperatures will be required.

A second path to metallization of hydrogen is at high temperature and pressure in the liquid phase. This region is called hot-dense matter and is of particular interest to planetary scientists; these are the conditions found in the giant outer planets and exoplanets where the dense matter can exist as a plasma. A plasma is a fluid with ionized atoms or molecules. In a fluorescent lamp, a low-density, low-temperature gas of atoms is ionized by an applied electric field. At high enough temperatures and pressures in a gas or liquid, a plasma can be formed because a certain portion of the particles are thermally ionized and the condensed matter system can electrically conduct. The article by Morales et al. (2) in PNAS predicts a first-order phase transition to a metallic phase of liquid atomic hydrogen at high pressure and temperature. This is the so-called plasma-phase transition (PPT). A possible phase diagram of hydrogen is shown in Fig. 1.

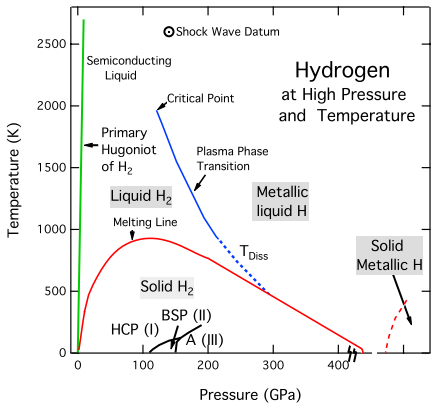

Fig. 1. A possible phase diagram for hydrogen, showing the theoretical melting line and the plasma-phase transition line. At lower temperatures in the solid, three phases are observed: hexagonal close packed (HCP), the broken symmetry phase (BSP), and the hydrgrogen A phase (sometimes called I, II, and III). Hydrogen may be liquid-atomic metallic at very high pressure and $T = 0$ K, shown by the extrapolations (dotted lines). At even higher pressures, the atomic liquid would solidify. A single shock wave generates points on the primary Hugoniot, with very high temperatures but modest pressures; higher pressures and lower temperatures are achieved off-Hugoniot with a reverberating shock wave. The dash-dot line is an isochore.

Theoretical studies have various degrees of sophistication, and because predictions of properties of hydrogen have had a number of conflicting results, it is useful to classify these. Most modern studies of hydrogen use Monte Carlo or molecular-dynamics simulations requiring substantial computing resources. Here, a large number of particles are allowed to collide or interact with each other until they achieve an equilibrium phase. The least demanding approach is to use effective pair potentials for each density, but these do not accurately handle the many-body problem. Next is Born-Oppenheimer molecular dynamics (BOMD), in which, at each density, the energetics are calculated using density functional theory (DFT). DFT has reasonable accuracy and puts increased demand on computational requirements. A weakness for hydrogen is that DFT does not handle zero-point motion and underestimates energy bandgaps, important for insulator-metal transitions. Quantum Monte Carlo (QMC) is more accurate but more demanding on computational requirements; it provides a complete quantum mechanical handling of the electron-ion interaction, and Morales et al. (2) use a modification called coupled electron-ion Monte Carlo (CEIMC), with the motion of the nuclei being treated classically. Finally, path-integral Monte Carlo (PIMD) treats all particles quantum mechanically and is the most demanding for computational resources.

Interest in the high-temperature path to metallic hydrogen has grown in recent years. A theoretical analysis by Scandolo (3) and Bonev et al. (4) predicted a peak in the melting line of hydrogen and above this, a line of dissociation to a non-molecular liquid; the peak in the melting line has been observed in static high-pressure experiments. With increasing pressure beyond the peak, the melting temperature decreases. Theory is not yet able to handle the low-temperature regime at high pressure, but if extrapolated, the melting line may intersect the pressure axis at several megabars (Fig.1, dotted line). Also, by extrapolation, the line for the transition from liquid-molecular to liquid-atomic phase intersects the melting line so that for higher P, solid molecular hydrogen melts to liquid-atomic hydrogen. This transition from molecular liquid to atomic liquid is called the PPT (discussed below). However, in a more recent theoretical paper, Tamblyn and Bonev (5) focused on the degree of dissociation and do not observe a first-order phase transition. Earlier studies of hot-dense hydrogen using the CEIMC approach did not detect a first-order phase transition. In the paper by Morales et al. (2), a finer P,T and density grid are used, and the PPT is observed in three approximations: BOMD, CEIMC, and PIMC. PIMC was only used in a limited P-T range. They also calculate the electrical conductivity, which has the appearance of an order parameter for the insulator-metal transition, although it is a transport property (2).

What is a metal, and what is the PPT? At low density, atoms or molecules are far apart with little overlap, and electrons are localized on the atoms so that the system is insulating. As the density increases, an insulating crystalline solid becomes semiconducting with an energy gap between the valence and conduction

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bands; the gap energy is required to excite an electron into the conduction band, thus conductivity is 0 at $T = 0$ K. At sufficiently high density and overlap of atoms, the gap closes, and the electrons become delocalized in the conduction band. At $T = 0$ K, the electrons can conduct, and the system of atoms is a metal. A rigorous experimental test for a metal is to show that the electrical conductivity is finite in the $T = 0$ K limit. This test cannot be carried out for a liquid, because there is no known liquid metal at $T = 0$ K. Now consider hot-dense matter of an atomic system such as xenon or helium in the fluid phase. As temperature and density increase, the fluid goes from insulating state to semiconducting state to ionized plasma, and conducting state. With further increase, rather than a continuous change, a first-order phase transition is predicted to take place, with an abrupt change in density and degree of ionization. If the atomic overlap is sufficient, the highly ionized state may also be a metal; the term PPT has been used whether metal or not. The insulator–metal transition is characterized by a certain value of the direct current electrical conductivity (Mott minimum conductivity). Landau and Zeldovich (6) first discussed such a transition in the Soviet literature in 1943; Norman and Starostin carried out calculations of the PPT in 1968 (7) and 1970 (8). The PPT, predicted to have a critical point, has never been definitively observed experimentally.

Hydrogen has an added consideration: it is molecular. Although not the first paper, a detailed discussion of the PPT was presented by Saumon and Chabrier in 1992 (9). The PPT was predicted to occur along with a dissociation transition from the molecular to the atomic metallic phase, first occurring at a temperature ~15,000 K at the critical point. However, more recently, they did not find support for the PPT in their effective field model (10). The PPT is now again predicted, in the work of Morales et al. (2), at much lower temperatures.

Morales et al. predict the PPT on three different quantum models.

Until now, experimental attempts to observe the PPT have been with shock waves. Weir et al. (11) used a reverberating shock wave; the high P,T conditions exist for a few hundred nanoseconds. Hydrogen was compressed to ~140 GPa, and temperatures were estimated to be around 3,000 K (see point in Fig. 1). Their measured conductivity is consistent with DC values calculated for liquid-atomic metallic hydrogen by Morales et al. (2); however, they do not observe a discontinuity, a property of the PPT. Fortov et al. (12) also used reverberating shock waves to compress deuterium and report a large-density step at P ~ 150 GPa and T ~ 4,000 K. However, in this challenging experiment, their data are sparse, conductivity seems to be measured on another sample, and temperature and pressure are calculated, and therefore, this does not provide strong evidence of the PPT.

It is interesting to consider an isochore, shown in Fig. 1. The ionization or metallization and the dissociation seem to be intimately connected. Because the phase lines have a negative slope, the density increases as the lines are crossed with increasing temperature; within a phase, the pressure increases because of increased thermal pressure. Although the atomic density is constant, in transcending from liquid H_2 to atomic H, there are two times as many particles when molecules dissociate, which results in increased overlap of the particle wave functions, a condition needed for metallization.

Theoretical studies of hydrogen have become increasingly more sophisticated, and now, Morales et al. (2) predict the PPT on three different quantum models. It will be important and challenging to achieve strong experimental confirmation of the phase diagram of hydrogen and its isotopes in the region of hot-dense matter.

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1. Wigner E, Huntington HB (1935) On the possibility of a metallic modification of hydrogen. *J Chem Phys* 3: 764–770.
2. Morales MA, Pierleoni C, Schwegler E, Ceperley DM (2010) Evidence for a first order liquid–liquid transition in high pressure hydrogen from ab-initio simulations. *Proc Natl Acad Sci* 107:12799–12803.
3. Scandolo S (2003) Liquid–liquid phase transition in compressed hydrogen from first-principles simulations. *Proc Natl Acad Sci USA* 100:3051–3053.
4. Bonev SA, Schwegler E, Ogitsu T, Galli G (2004) A quantum fluid of metallic hydrogen suggested by first-principles calculations. *Nature* 431:669–672.
5. Tamblyn I, Bonev SA (2010) Structure and phase boundaries of compressed liquid hydrogen. *Phys Rev Lett* 104: 065702.
6. Landau LD, Zeldovich YB (1943) On the relation between the liquid and the gaseous states of metals. *Acta Physico-Chimica U.R.S.S.* 18:380.
7. Norman GE, Starostin AN (1968) *Teplofiz Vys Temp* 6 (1968):410.
8. Norman GE, Starostin AN (1970) *Teplofiz Vys Temp* 8:413.
9. Saumon D, Chabrier G (1992) Fluid hydrogen at high density: Pressure ionization. *Phys Rev A* 46:2084–2100.
10. Chabrier G, Saumon D, Wiisdoerffer C (2007) Hydrogen and helium at high density and astrophysical implications. *Astrophys Space Sci* 307:263–267.
11. Weir ST, Mitchell AC, Nellis WJ (1996) Metallization of fluid molecular hydrogen at 140 GPa (1.4 Mbar). *Phys Rev Lett* 76:1860–1863.
12. Fortov VE, et al. (2007) Phase transition in a strongly nonideal deuterium plasma generated by quasi-isentropical compression at megabar pressures. *Phys Rev Lett* 99: 185001–185004.